

[JP,2002-309119,A]

Japanese (PDF)

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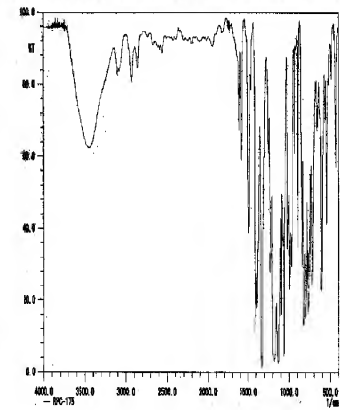
- Notes:
- 1. Untranslatable words are replaced with asterisks (***) .
 - 2. Texts in the figures are not translated and shown as it is.

Translated: 01:02:30 JST 01/01/2010
Dictionary: Last updated 12/14/2009 / Priority: 1. Chemistry / 2. Electronic engineering

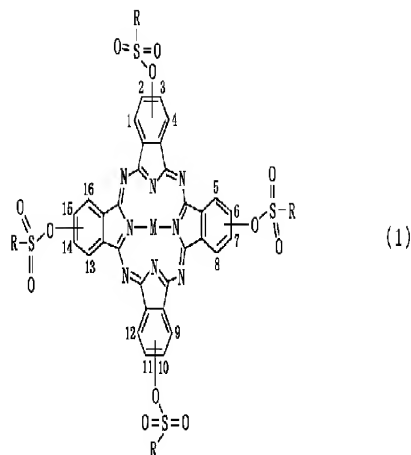
CLAIM + DETAILED DESCRIPTION

[Claim(s)]
[Claim 1]A phthalocyanine compound characterized by what is denoted by a following general formula (1).
[Chemical formula 1]

Drawing selection **Drawing 1**



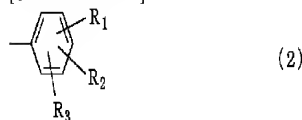
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() [among a formula] [R] [an aryl group which may have an alkyl group which may have a substituent, or a substituent of the carbon numbers 1-4] [express and] M expresses Cu, nickel, Co, Zn, Pd, Cd, VO, or TiO, The numbers 1-16 of the phthalocyanine skeleton circumference showed a location number of a carbon atom, and an oxygen atom of substituent $R(O=)_2SO-$ is combined with four carbon atoms chosen, respectively from either [either / either / either 1-4 and / 5-8 and / 9-12 and] 13-16.

[Claim 2] R is an aryl group denoted by a following general formula (2), and M Cu, nickel, Are either Co, Zn, Pd, Cd, VO or TiO, and an oxygen atom of substituent $R(O=)_2SO-$ Either 1-4. The phthalocyanine compound according to claim 1 having combined with four carbon atoms chosen, respectively from either [either / either 5-8 and / 9-12 and] 13-16.

[Chemical formula 2]



(R_1 , R_2 , and R_3 express independently an alkyl group of a hydrogen atom, a halogen atom, and the carbon numbers 1-4, or a fluorine substituted alkyl group of the carbon numbers 1-4 among a formula, respectively)

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the new phthalocyanine compound which can be used for the pigment for optical record, the pigment for light filters, a photoelectric transducer, an electro

photography photo conductor, an organic semiconductor element, a catalyst and a gas sensor, and a light filter. This invention relates to a new phthalocyanine compound suitable as a pigment for CD-R which is a compact disc which can be added especially in more detail.

[0002]

[Description of the Prior Art]CD (compact disc) as a recording medium and the demand of CD-R (compact disc which can be added) are growing remarkably with information machines and equipment in recent years or development of communication environments. CD-R is CD and a compatible added type recording medium of a postscript, and improvement in the speed of a recording rate is further called for increasingly as frequency in use increases, while the low price of the byte unit price and the simplicity of operation are accepted and a market is expanded.

[0003]Using phthalocyanine as a pigment for optical record is widely known by JP,7-56019,B etc.

However, in these Prior arts, the more it gathers a recording rate, the thermal interference during a record mark (pit) or between tracks (guide rail called a groove) increases, and, the more there is a problem that record becomes difficult. Although CD-R records information by carrying out the pyrolysis of the organic coloring matter contained in a recording layer using a laser beam, it is because modification of a recording layer will take place superfluously and even places other than the target place will change, when high-speed record is irradiated with the laser beam of high energy. In order to solve this problem, the pigment disassembled with sufficient heat responsibility at high speed is called for, but that of a stake of the pigment which has such characteristics with organic coloring matter is the actual condition obtaining. Many of what has quick catabolic rate is because decomposition takes place explosively, so the range which the influence attains to tends to become large with a pigment.

[0004]This invention persons have already proposed the pigment as shown in JP,10-45761,A, JP,11-49773, A, etc. as phthalocyanine dye for optical record, and, [these pigments] the high solubility to an organic solvent -- high -- a sensitivity recording characteristic, high light stability, etc. have character suitable as a pigment for CD-R. However, realization of the recording material which can respond to this with the demand of improvement in the speed from that of the recording rate of CD-R as mentioned above is called for.

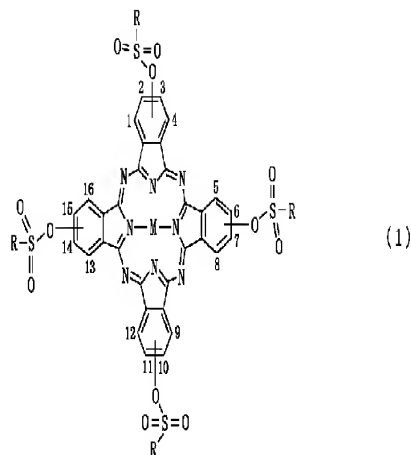
[0005]

[Problem to be solved by the invention]This invention makes it the SUBJECT to provide the new phthalocyanine compound which has character suitable as pigments for CD-R, such as high solubility to an organic solvent, a recording characteristic recordable high-speed which is high sensitivity, high light stability, in view of this actual condition.

[0006]

[Means for solving problem]This invention persons came to complete this invention, as a result of repeating examination, in order to solve above-mentioned SUBJECT and to realize improvement in the speed of record further. That is, according to this invention, the phthalocyanine compound characterized by what is denoted by a following general formula (1) is provided.

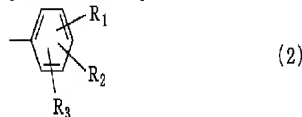
[Chemical formula 3]



() [among a formula] [R] [the aryl group which may have the alkyl group which may have a substituent, or a substituent of the carbon numbers 1-4] [express and] M expresses Cu, nickel, Co, Zn, Pd, Cd, VO, or TiO, The numbers 1-16 of the phthalocyanine skeleton circumference showed the location number of the carbon atom, and the oxygen atom of substituent $R(O=)_2SO-$ is combined with four carbon atoms chosen, respectively from either [either / either / either 1-4 and / 5-8 and / 9-12 and] 13-16.

[0007]According to this invention, it is an aryl group as which R is expressed in a following general formula (2) in the above-mentioned composition, M is either Cu, nickel, Co, Zn, Pd, Cd, VO or TiO, A phthalocyanine compound, wherein the oxygen atom of substituent $R(O=)_2SO-$ has combined with four carbon atoms chosen, respectively from either [either / either / either 1-4 and / 5-8 and / 9-12 and] 13-16 is provided.

[Chemical formula 4]

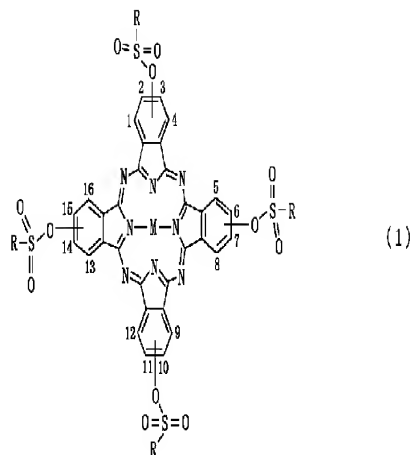


(R_1 , R_2 , and R_3 express independently the alkyl group of a hydrogen atom, a halogen atom, and the carbon numbers 1-4, or the fluorine substituted alkyl group of the carbon numbers 1-4 among a formula, respectively)

[0008]

[Mode for carrying out the invention]This invention is explained in detail below. The new phthalocyanine compound by this invention is denoted by a following general formula (1).

[Chemical formula 5]



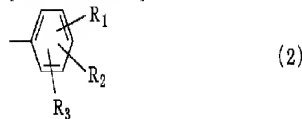
() [among a formula] [R] [the aryl group which may have the alkyl group which may have a substituent, or a substituent of the carbon numbers 1-4] [express and] M expresses Cu, nickel, Co, Zn, Pd, Cd, VO, or TiO, The numbers 1-16 of the phthalocyanine skeleton circumference showed the location number of the carbon atom, and the oxygen atom of substituent R(O=)₂SO- is combined with four carbon atoms chosen,

respectively from either [either / either / either 1-4 and / 5-8 and / 9-12 and] 13-16.

[0009][the phthalocyanine compound of the desirable form of this invention] It is an aryl group as which R is expressed in a following general formula (2) in the phthalocyanine compound denoted by the above-mentioned general formula (1), M is either Cu, nickel, Co, Zn, Pd, Cd, VO or TiO, and the oxygen atom of substituent R(O=)₂SO- has combined with four carbon atoms chosen, respectively from either [either /

either / either 1-4 and / 5-8 and / 9-12 and] 13-16.

[Chemical formula 6]



(R₁, R₂, and R₃ express independently the alkyl group of a hydrogen atom, a halogen atom, and the carbon numbers 1-4, or the fluorine substituted alkyl group of the carbon numbers 1-4 among a formula, respectively)

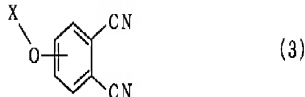
[0010]The phthalocyanine compound concerning this invention has a carboxylate group as a substituent. According to the effect of these substituents, the pigment of this invention shows low decomposition temperature.

[0011]The phthalocyanine compound concerning this invention is a compound denoted by the above-mentioned general formula (1), and, [as an example of the substituent R] For example, an alkyl group, an alkoxyalkyl group, a perfluoroalkyl group, a fluorine substituted alkyl group, the phenyl group that may

have a substituent, the naphthyl group which may have a substituent, etc. are mentioned. [as an example of a phenyl group and the substituent of a naphthyl group] For example, a fluorine atom, a chlorine atom, a bromine atom, or the halogen atom of iodine atoms, A methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl group, Alkyl groups, such as a tert-butyl group and an isobutyl group, a methoxy group, Alkoxy groups, such as an ethoxy group, n-propoxy group, an isopropoxy group, and an n-butoxy group, Alkoxy substituted alkyl groups, such as a polyfluoroalkoxy group [such as polyfluoro alkyl groups, such as a trifluoromethyl group, a 2,2,2-trifluoroethoxy group, and a 2,2,3,3,3-pentafluoro propoxy group,], methoxy ethyl group, and ethoxyethyl group, etc. are mentioned.

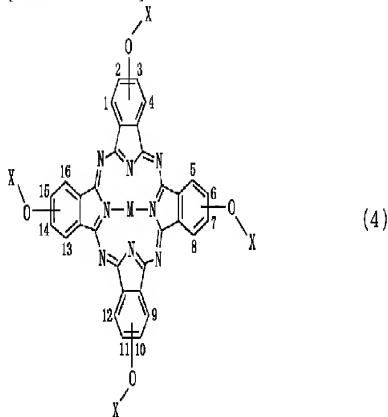
[0012]The phthalocyanine compound denoted by the above-mentioned general formula (1) cyclizes the phthalonitrile compound which has an alkoxy group as shown with a following general formula (3), and compounds the phthalocyanine compound shown with a following general formula (4). Subsequently, by applying this to an alkoxy cleavage reaction, a tetrahydroxy phthalocyanine compound as shown with a following general formula (5) can be compounded, and it can compound by making acid halide react to this compound, respectively.

[Chemical formula 7]



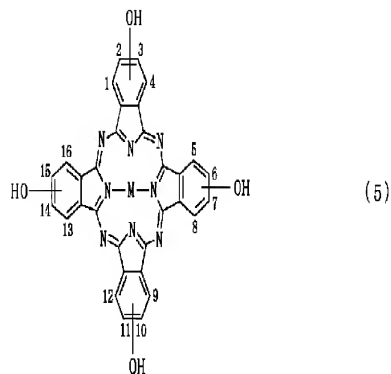
(X express among a formula the alkyl group which may have a substituent)

[Chemical formula 8]



(X have the same meaning as the above-mentioned general formula (3) among a formula, and the numbers 1-16 of the phthalocyanine skeleton circumference express the location number of the carbon atom)

[Chemical formula 9]



[0013]The phthalonitrile compound shown by the above-mentioned general formula (3) can be obtained by making a publicly known alcohol derivative and nitrophthalonitrile, or halogenation phthalonitrile react under publicly known conditions. In order to obtain the phthalocyanine compound which cyclizes the phthalonitrile compound shown by the above-mentioned general formula (3), and is shown by the above-mentioned general formula (4), 1, 8-diazabicyclo [5.4.0]-7-undecene (DBU) which are organic bases in required metal salt about the phthalonitrile compound shown by the above-mentioned general formula (3), 1,5-diazabicyclo [4.3.0]-5-nonene (DBN), sodium alcoholate, What is necessary is just to make it react under existence of potassium alkoxide etc. in alcohol solvents, such as methanol, ethanol, propanol, butanol, pentanol, methoxy ethanol, and ethoxyethanol and ethoxypropanol. In this reaction, a reaction can also be smoothly advanced using the substance which may generate ammonia, such as ammonia, formamide, urea, for example.

[0014]What is necessary is just to cover the phthalocyanine compound shown by the above-mentioned general formula (4) over an alkoxy cleavage reaction, in order to obtain the tetrahydroxy phthalocyanine compound shown by the above-mentioned general formula (5) from the phthalocyanine compound shown by the above-mentioned general formula (4). How to heat in a pyridinehydrochloride the phthalocyanine compound shown by the above-mentioned general formula (4) as a general method, for example, There is a method of making it react to boron tribromide in organic solvents, such as benzene, toluene, dichloromethane, or carbon tetrachloride, or the method of making it react to sodiumthiolate in DMF.

[0015][the phthalocyanine compound shown by the above-mentioned general formula (1)] The tetrahydroxy phthalocyanine compound and acid halide which are shown by the above-mentioned general formula (5) THF, Dioxane, DMF, DMSO, DMI, dimethylacetamide, N-methyl-2-pyrrolidone, The inside of aprotic polar solvents, such as acetonitrile and hexamethylphosphoric triamide, Sodium hydride, potassium hydride, triethylamine, tributylamine, Pyridine, N-methyl morpholine, DBU, DBN, N,N,N',N'-tetramethylethylenediamine, What is necessary is just to make it react under existence of bases, such as N, N,N',N'-tetramethyl 1,3-propanediamine, a N,N,N',N'-tetramethyl 1,4-butanediamine, and N,N,N',N'-tetramethyl 1,6-hexanediamine.

[0016]The range and many whose degradation starting temperatures of the phthalocyanine compound denoted by the above-mentioned general formula (1) produced by performing it above are 100-400 ** are

within the limits of 250-350 **, and this is suitable as decomposition temperature of the pigment for CD-R. If decomposition temperature is more high, recording sensitivity will worsen, and if decomposition temperature is too low, a heat-resisting property will worsen.

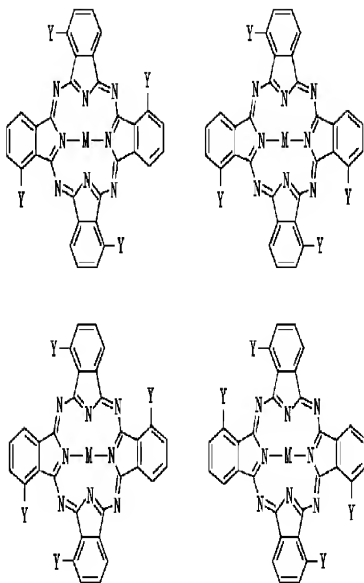
[0017] Since the phthalocyanine compound denoted by the above-mentioned general formula (1) has the good solubility to an organic solvent, it dissolves in a suitable organic solvent, and by carrying out a spin coat, it can be thin-film-ized easily and can be used as a recording layer. They may be used independently, and these phthalocyanine compounds may form a recording layer, and two or more sorts may be mixed and it may be used for them. Or it may mix with a phthalocyanine compound which is indicated by the compound except this invention showing, for example, said JP,10-45761,A, JP,11-49773,A, etc., and may use.

[0018]

[Working example] Hereafter, an embodiment explains this invention still more concretely. The structure of the compound obtained in these embodiments is shown in after-mentioned Table 1 and 2. Although the substituent of a phthalocyanine compound is shown by the following explanation, the display "alpha" and "beta" may be used. Although the phthalocyanine skeleton has the form which four benzene ring condensed on the outside of the tetraaza porphyrin skeleton, each benzene-ring portion has a place into which a substituent can go four places at a time. Among these, an alpha position and two distant positions are called beta for two positions near a tetraaza porphyrin skeleton. For example, if the phthalonitrile compound in which the 3rd place was substituted is cyclized, the phthalocyanine compound containing a substituent will generate to an alpha position, but it is four sorts of following isomeric mixtures. In operation of explaining below, since it is a mixture of these four following sorts of isomers, these isomeric mixtures are dealt with collectively, but it is also possible to dissociate, respectively and to use if needed.

[0019]

[Chemical formula 10]



(Y expresses a substituent among a formula.)

[0020]Embodiment 1: Synthetic (1)3-methoxy phthalonitrile of alpha, alpha, alpha, and alpha-tetrakis [4-(trifluoromethyl) phenylsulfonyloxy] vanadyl phthalocyanine (compound 1) (intermediate of the compound 1)

86.5 g of 3-nitrophthalonitrile, the methanol 19.2g, the anhydrous potassium carbonate 165.6g, and DMSO350ml were taught to the reaction flask which attached the condenser tube, and it agitated at 65 °C under the nitrogen air current for 4 hours. The reaction mixture was discharged in 2000 ml of water, and the precipitated crystal was separated, and it washed, dried [heating and churning were stopped, and], and the 66.4 g (84.1% of yield) purpose compound was obtained. As a result of conducting GC/MS analysis of this compound, molecular ion peak M+=158 was checked.

(2) alpha, alpha, alpha, and alpha-tetramethoxy vanadyl phthalocyanine (intermediate of the compound 1) 19.8 g of 3-methoxy phthalonitrile obtained above (1), 8.50 g of sodium methoxide, 6.00 g of formamide, and 188 ml of 1-pentanol were taught, it heated and temperature up was carried out to the reaction flask which attached the condenser tube. 6.45 g of vanadium trichloride was added at 90 °C, nitrogen gas was introduced, and it agitated at 90-100 °C for 5 hours. stopping heating and churning and discharging a reaction mixture in 2000 ml of methanol -- a crystal -- separation and methanol -- subsequently it washed and dried with acetone and 21.9-g crude pigments were obtained. 10.0 g of this crude pigment was extracted, separation refinement was carried out with column chromatography (a silica gel/chloroform: THF=15:1-4:1), and the 3.86-g purpose pigment was obtained.

(3) alpha, alpha, alpha, and alpha-tetrahydroxy vanadyl phthalocyanine (precursor of the compound 1) 110.6 g of pyridine was taught to the reaction flask which attached the condenser tube, and 146.0 g of

concentrated hydrochloric acid was dropped, agitating during an ice water bath. After distilling off water completely in vacuum distillation, the phthalocyanine compound 8.46g which carried out temperature up and was obtained above (2) to 100 °C was added, and it agitated at 200-210 °C for 4 hours. Heating was stopped and this was diluted with hydrochloric acid 10% in the place where the temperature of the reaction mixture became 110 °C. After agitating for 1 hour, acetone washed [separation, a flush, and] the precipitated crystal, it dried, and the 6.00-g purpose pigment was obtained.

(4) alpha, alpha, alpha, and alpha-tetrakis [4-(trifluoromethyl) phenylsulfonyloxy] vanadyl phthalocyanine (compound 1)

0.41 g of sodium hydride (60% oil suspension) was added teaching and agitating the phthalocyanine compound 0.75g and anhydrous THF10ml which was obtained above (3) in the reaction flask which attached the condenser tube, and it agitated at 40 °C for 10 minutes. 2.52 g of 4-(trifluoromethyl) benzenesulphonyl chloride was added there, and it agitated at 50-55 °C for 120 hours. Heating and churning were stopped and the reaction mixture was diluted with 100 ml of methanol, and methanol/water (1/1) washed [separation and] the crystal which trickled 20 ml of water and deposited, it dried, and 1.62-g crude pigments were obtained. Separation refinement of this crude pigment was carried out with column chromatography (activated alumina/toluene: ethyl acetate =100:1-50:1), and 0.56-g refining pigments were obtained. lambda_{max} in the inside of chloroform of this phthalocyanine compound was 703 nm. The extrapolation loss-in-quantity starting temperature measured by TG analysis was 293 °C, the extrapolation exothermic starting temperature measured by DSC analysis was 280 °C, and the calorific power of the half band width of 109 J/g and an exothermic peak was 13 °C. Each of these thermal analyses is measured under a nitrogen air current, and is the same also about the thermal-analysis value of other embodiments. As a result of conducting LC/MS analysis of this compound, molecular ion peak M⁺=1474 was checked. An IR spectrum is shown in [drawing 1](#). The ultimate-analysis value was as follows.

C(%) H(%) N(%) F(%)

Actual measurement 48.82 1.917.59 15.44 calculated value 48.85 1.90 7.60 15.46 (as

C₆₀H₂₈F₁₂N₈O₁₃S₄V=1474)

[0021]Embodiment 2: alpha, alpha, alpha, and alpha-tetrakis (phenylsulfonyloxy) vanadyl phthalocyanine (compound 2)

0.41 g of sodium hydride (60% oil suspension) was added teaching and agitating the phthalocyanine compound 0.75g and anhydrous THF10ml which was obtained by (3) of Embodiment 1 in the reaction flask which attached the condenser tube, and it agitated at 40 °C for 10 minutes. 1.82 g of benzenesulphonyl chloride was added there, and it agitated at 50-55 °C for 100 hours. The reaction mixture was diluted with 100 ml of methanol, and methanol washed [separation and] the precipitated crystal, it dried [heating and churning were stopped, and], and 1.35-g crude pigments were obtained. Separation refinement of this crude pigment was carried out with column chromatography (activated alumina/toluene: ethyl acetate =50:1), and 0.31-g refining pigments were obtained. lambda_{max} in the inside of chloroform of this phthalocyanine compound was 702 nm. The extrapolation loss-in-quantity starting temperature measured by TG analysis was 289 °C, the extrapolation exothermic starting temperature measured by DSC analysis was 275 °C, and the calorific power of the half band width of 228 J/g and an exothermic peak was 11 °C. As a result of conducting LC/MS analysis of this compound, molecular ion peak M⁺=1203 was

checked. The ultimate-analysis value was as follows.

	C (%)	H (%)	N (%)
実測値	55.89	2.68	9.30
計算値	55.85	2.66	9.31

(as C56H32N8O13S4V=1203)

[0022]Embodiment 3: alpha, alpha, alpha, and alpha-tetrakis (p-toluenesulfonyloxy) vanadyl phthalocyanine (compound 3)

0.41 g of sodium hydride (60% oil suspension) was added teaching and agitating the phthalocyanine compound 0.75g and anhydrous THF10ml which was obtained by (3) of Embodiment 1 in the reaction flask which attached the condenser tube, and it agitated at 40 ** for 10 minutes. 1.82 g of p-tosyl chloride was added there, and it agitated at 50-55 ** for 100 hours. The reaction mixture was diluted with 100 ml of methanol, and methanol washed [separation and] the precipitated crystal, it dried [heating and churning were stopped, and], and 1.35-g crude pigments were obtained. Separation refinement of this crude pigment was carried out with column chromatography (activated alumina/toluene: ethyl acetate =50:1), and 0.31-g refining pigments were obtained. lambdamax in the inside of chloroform of this phthalocyanine compound was 702 nm. The extrapolation loss-in-quantity starting temperature measured by TG analysis was 289 **, the extrapolation exothermic starting temperature measured by DSC analysis was 275 **, and the calorific power of the half band width of 228 J/g and an exothermic peak was 11 **. As a result of conducting LC/MS analysis of this compound, molecular ion peak M+=1259 was checked. The ultimate-analysis value was as follows.

	C (%)	H (%)	N (%)
実測値	57.20	3.16	8.88
計算値	57.19	3.18	8.90

(as C60H40N8O13S4V=1259)

[0023]Embodiment 4: alpha, alpha, alpha, and alpha-tetrakis (2,4,6-trimethyl phenyl sulfonyloxy) vanadyl phthalocyanine (compound 4)

0.25 g of sodium hydride (60% oil suspension) was added teaching and agitating the phthalocyanine compound 0.50g and anhydrous THF6ml which was obtained by (3) of Embodiment 1 in the reaction flask which attached the condenser tube, and it agitated at 40 ** for 10 minutes. 1.36 g of 2,4,6-bird methylbenzene sulfonyl chloride was added there, and it agitated at 50-55 ** for 124 hours. The reaction mixture was diluted with 100 ml of methanol, and methanol washed [separation and] the precipitated crystal, it dried [heating and churning were stopped, and], and 0.89-g crude pigments were obtained. Separation refinement of this crude pigment was carried out with column chromatography (activated alumina/toluene: ethyl acetate =100:1-50:1), and 0.38-g refining pigments were obtained. lambdamax in the inside of chloroform of this phthalocyanine compound was 705 nm. The extrapolation loss-in-quantity starting temperature measured by TG analysis was 269 **, the extrapolation exothermic starting temperature measured by DSC analysis was 253 **, and the calorific power of the half band width of 155 J/g and an exothermic peak was 10 **. As a result of conducting LC/MS analysis of this compound,

molecular ion peak M+=1371 was checked. The ultimate-analysis value was as follows.

	C (%)	H (%)	N (%)
実測値	59.50	4.10	8.16
計算値	59.52	4.08	8.17

(as C68H56N8O13S4V=1371)

[0024]Embodiment 5: alpha, alpha, alpha, and alpha-tetrakis (2,4,6-triisopropyl phenylsulfonyloxy) vanadyl phthalocyanine (compound 5)

0.27 g of sodium hydride (60% oil suspension) was added teaching and agitating the phthalocyanine compound 0.50g and anhydrous THF10ml which was obtained by (3) of Embodiment 1 in the reaction flask which attached the condenser tube, and it agitated at 40 ** for 10 minutes. 2.07 g of 2,4,6-triisopropyl benzenesulfonyl chloride was added there, and it agitated at 50-55 ** for 100 hours. The reaction mixture was diluted with 100 ml of methanol, and methanol washed [separation and] the precipitated crystal, it dried [heating and churning were stopped, and], and 0.86-g crude pigments were obtained. Separation refinement of this crude pigment was carried out with column chromatography (activated alumina/toluene: ethyl acetate =100:1-50:1), and 0.13-g refining pigments were obtained. lambdamax in the inside of chloroform of this phthalocyanine compound was 700 nm. The extrapolation loss-in-quantity starting temperature measured by TG analysis was 267 **, the extrapolation exothermic starting temperature measured by DSC analysis was 245 **, and the calorific power of the half band width of 51 J/g and an exothermic peak was 20 **. As a result of conducting LC/MS analysis of this compound, molecular ion peak M+=1707 was checked. The ultimate-analysis value was as follows.

	C (%)	H (%)	N (%)
実測値	64.65	6.07	6.55
計算値	64.67	6.09	6.56

(as C92H104N8O13S4V=1707)

[0025]Embodiment 6: alpha, alpha, alpha, and alpha-tetrakis (4-chlorophenyl sulfonyloxy) vanadyl phthalocyanine (compound 6)

0.27 g of sodium hydride (60% oil suspension) was added teaching and agitating the phthalocyanine compound 0.50g and anhydrous THF6ml which was obtained by (3) of Embodiment 1 in the reaction flask which attached the condenser tube, and it agitated at 40 ** for 10 minutes. 1.44 g of 4-chlorobenzene sulfonyl chloride was added there, and it agitated at 50-55 ** for 114 hours. The reaction mixture was diluted with 100 ml of methanol, and methanol washed [separation and] the precipitated crystal, it dried [heating and churning were stopped, and], and 0.95-g crude pigments were obtained. Separation refinement of this crude pigment was carried out with column chromatography (activated alumina/toluene: ethyl acetate =100:1-50:1), and 0.23-g refining pigments were obtained. lambdamax in the inside of chloroform of this phthalocyanine compound was 701 nm. The extrapolation loss-in-quantity starting temperature measured by TG analysis was 291 **, the extrapolation exothermic starting temperature measured by DSC analysis was 264 **, and the calorific power of the half band width of 196 J/g and an exothermic peak was 15 **. As a result of conducting LC/MS analysis of this compound, molecular ion

peak M+=1340 was checked. The ultimate-analysis value was as follows.

	C (%)	H (%)	N (%)
実測値	50.11	2.14	3.35
計算値	50.15	2.16	8.36

(as C56H28Cl4N8O13S4V=1340)

[0026]Embodiment 7: alpha, alpha, alpha, and alpha-tetrakis (4-tert-butylphenyl sulfonyloxy) vanadyl phthalocyanine (compound 7)

0.27 g of sodium hydride (60% oil suspension) was added teaching and agitating the phthalocyanine compound 0.50g and anhydrous THF10ml which was obtained by (3) of Embodiment 1 in the reaction flask which attached the condenser tube, and it agitated at 40 ** for 10 minutes. 1.59 g of 4-tert-butylbenzene sulfonyl chloride was added there, and it agitated at 50-55 ** for 100 hours. The reaction mixture was diluted with 100 ml of methanol, and methanol washed [separation and] the precipitated crystal, it dried [heating and churning were stopped, and], and 0.86-g crude pigments were obtained. Separation refinement of this crude pigment was carried out with column chromatography (activated alumina/toluene: ethyl acetate =100:1-50:1), and 0.18-g refining pigments were obtained. lambdamax in the inside of chloroform of this phthalocyanine compound was 703 nm. The extrapolation loss-in-quantity starting temperature measured by TG analysis was 295 **, the extrapolation exothermic starting temperature measured by DSC analysis was 284 **, and the calorific power of the half band width of 215 J/g and an exothermic peak was 10 **. As a result of conducting LC/MS analysis of this compound, molecular ion peak M+=1427 was checked. The ultimate-analysis value was as follows.

	C (%)	H (%)	N (%)
実測値	60.54	4.46	7.83
計算値	60.55	4.48	7.85

(as C72H64N8O13S4V=1427)

[0027]Embodiment 8: alpha, alpha, alpha, and alpha-tetrakis [2-(1-butoxy)-5-methylphenyl sulfonyloxy] vanadyl phthalocyanine (compound 8)

The phthalocyanine compound 1.00g obtained by (3) of Embodiment 1 in the reaction flask which attached the condenser tube, 4.29 g of N,N,N',N'-tetramethyl 1,6-hexanediamine and 15 ml of N-methyl-2-pyrrolidone were taught, and 4.00 g of 2-(1-butoxy)-5-methylbenzene sulfonyl chloride was dropped over 2 hours, agitating under cooling in an ice water bath. After termination of dropping, the temperature of the reaction mixture was returned to the room temperature, and was agitated for 80 hours. The reaction mixture was diluted with 100 ml of methanol, and methanol washed [separation and] the precipitated crystal, it dried [churning was stopped, and], and 1.90-g crude pigments were obtained. Separation refinement of this crude pigment was carried out with column chromatography (activated alumina/chloroform: ethyl acetate =50:1), and 1.10-g refining pigments were obtained. lambdamax in the inside of chloroform of this phthalocyanine compound was 705 nm. The extrapolation loss-in-quantity starting temperature measured by TG analysis was 299 **, the extrapolation exothermic starting temperature measured by DSC analysis was 273 **, and the calorific power of the half band width of 60 J/g and an exothermic peak was 9 **. As a

result of conducting LC/MS analysis of this compound, molecular ion peak $M^+=1547$ was checked. The ultimate-analysis value was as follows.

	C (%)	H (%)	N (%)
実測値	58.93	4.66	7.22
計算値	58.95	4.65	7.24

(as C76H72N8O17S4V=1547)

[0028]Embodiment 9: alpha, alpha, alpha, and alpha-tetrakis [2-(1-butoxy)-5-tert-buthylphenyl sulfonyloxy] vanadyl phthalocyanine (compound 9)

The phthalocyanine compound 1.00g obtained by (3) of Embodiment 1 in the reaction flask which attached the condenser tube, 4.29 g of N,N,N',N'-tetramethyl 1,6-hexanediamine and 15 ml of N-methyl-2-pyrrolidone were taught, and 4.27 g of 2-(1-butoxy)-5-tert-butylbenzene sulfonyl chloride was supplied over 1 hour, agitating under cooling in an ice water bath. After the completion of an injection, the temperature of the reaction mixture was returned to the room temperature, and was agitated for 48 hours. Churning was stopped, the reaction mixture was diluted with 240 ml of methanol, the crystal which trickled 60 ml of water and deposited was taken, it washed and dried with methanol/water (6/1), and 1.55-g crude pigments were obtained. Separation refinement of this crude pigment was carried out with column chromatography (activated alumina/chloroform: ethyl acetate =300:1-250:1), and 1.20-g refining pigments were obtained. lambdamax in the inside of chloroform of this phthalocyanine compound was 704 nm. The extrapolation loss-in-quantity starting temperature measured by TG analysis was 290 **, the extrapolation exothermic starting temperature measured by DSC analysis was 263 **, and the calorific power of the half band width of 75 J/g and an exothermic peak was 10 **. As a result of conducting LC/MS analysis of this compound, molecular ion peak $M^+=1715$ was checked. The ultimate-analysis value was as follows.

	C (%)	H (%)	N (%)
実測値	61.55	5.57	6.50
計算値	61.57	5.60	6.53

(as C76H72N8O17S4V=1547)

[0029]Embodiment 10: alpha, alpha, alpha, and alpha-tetrakis (p-toluenesulfonyloxy) zinc phthalocyanine (compound 10)

- (1) alpha, alpha, alpha, and alpha-tetramethoxy zinc phthalocyanine (intermediate of the compound 10)
19.8 g of 3-methoxy phthalonitrile obtained by (1) of Embodiment 1, 8.50 g of sodium methoxide, 6.00 g of formamide, and 188 ml of 1-pentanol were taught, it heated and temperature up was carried out to the reaction flask which attached the condenser tube. The zinc chloride 6.04g was added at 90 **, nitrogen gas was introduced, and it agitated at 90-100 ** for 5 hours. stopping heating and churning and discharging a reaction mixture in 2000 ml of methanol -- a crystal -- separation and methanol -- subsequently it washed and dried with acetone and 19.0-g crude pigments were obtained. 10.0 g of this crude pigment was extracted, separation refinement was carried out with column chromatography (a silica gel/chloroform: THF=10:1-2:1), and the 6.98-g purpose pigment was obtained.
- (2) alpha, alpha, alpha, and alpha-tetrahydroxy zinc phthalocyanine (precursor of the compound 10)

110.6 g of pyridine was taught to the reaction flask which attached the condenser tube, and 146.0 g of concentrated hydrochloric acid was dropped, agitating during an ice water bath. After distilling off water completely in vacuum distillation, the phthalocyanine compound 6.98g which carried out temperature up and was obtained above (1) to 100 °C was added, and it agitated at 200-210 °C for 4 hours. Heating was stopped and this was diluted with hydrochloric acid 10% in the place where the temperature of the reaction mixture became 110 °C. After agitating for 1 hour, acetone washed [separation, a flush, and] the precipitated crystal, it dried, and the 5.50-g purpose pigment was obtained.

(3) alpha, alpha, alpha, and alpha-tetrakis (p-toluenesulfonyloxy) zinc phthalocyanine (compound 10)
The phthalocyanine compound 1.09g obtained by the above 3 in the reaction flask which attached the condenser tube, 4.29 g of N,N,N',N'-tetramethyl 1,6-hexanediamine and 15 ml of N-methyl-2-pyrrolidone were taught, and 2.61 g of p-tosyl chloride was supplied over 1 hour, agitating under cooling in an ice water bath. After the completion of an injection, the temperature of the reaction mixture was returned to the room temperature, and was agitated for 60 hours. The reaction mixture was diluted with 100 ml of methanol, and methanol washed [separation and] the precipitated crystal, it dried [churning was stopped, and], and 1.24-g crude pigments were obtained. Separation refinement of this crude pigment was carried out with column chromatography (activated alumina/chloroform: ethyl acetate =30:1-20:1), and 0.98-g refining pigments were obtained. lambda_{max} in the inside of chloroform of this phthalocyanine compound was 674 nm. As a result of conducting LC/MS analysis of the compound, molecular ion peak M⁺=1257 was checked.

[0030]Embodiment 11: alpha, alpha, alpha, and alpha-tetrakis (p-toluenesulfonyloxy) copper phthalocyanine (compound 11)

(1) alpha, alpha, alpha, and alpha-tetramethoxy copper phthalocyanine (intermediate of the compound 11)
19.8 g of 3-methoxy phthalonitrile obtained by (1) of Embodiment 1, 8.50 g of sodium methoxide, 6.00 g of formamide, and 188 ml of 1-pentanol were taught, it heated and temperature up was carried out to the reaction flask which attached the condenser tube. 4.38 g of copper(I) chlorides were added at 90 °C, nitrogen gas was introduced, and it agitated at 90-100 °C for 6 hours. stopping heating and churning and discharging a reaction mixture in 2000 ml of methanol -- a crystal -- separation and methanol -- subsequently it washed and dried with acetone and 18.5-g crude pigments were obtained. 10.0 g of this crude pigment was extracted, separation refinement was carried out with column chromatography (a silica gel/chloroform: THF=10:1-2:1), and the 7.23-g purpose pigment was obtained.

(2) alpha, alpha, alpha, and alpha-tetrahydroxy copper phthalocyanine (precursor of the compound 11)
110.6 g of pyridine was taught to the reaction flask which attached the condenser tube, and 146.0 g of concentrated hydrochloric acid was dropped, agitating during an ice water bath. After distilling off water completely in vacuum distillation, the phthalocyanine compound 7.23g which carried out temperature up and was obtained above (1) to 100 °C was added, and it agitated at 200-210 °C for 3 hours. Heating was stopped and this was diluted with hydrochloric acid 10% in the place where the temperature of the reaction mixture became 110 °C. After agitating for 1 hour, acetone washed [separation, a flush, and] the precipitated crystal, it dried, and the 5.00-g purpose pigment was obtained.

(3) alpha, alpha, alpha, and alpha-tetrakis (p-toluenesulfonyloxy) copper phthalocyanine (compound 11)
The phthalocyanine compound 1.00g obtained above (3) in the reaction flask which attached the condenser tube, 4.29 g of N,N,N',N'-tetramethyl 1,6-hexanediamine and 15 ml of N-methyl-2-pyrrolidone were

taught, and 2.61 g of p-tosyl chloride was supplied over 1 hour, agitating under cooling in an ice water bath. After the completion of an injection, the temperature of the reaction mixture was returned to the room temperature, and was agitated for 80 hours. The reaction mixture was diluted with 100 ml of methanol, and methanol washed [separation and] the precipitated crystal, it dried [churning was stopped, and], and 1.10-g crude pigments were obtained. Separation refinement of this crude pigment was carried out with column chromatography (activated alumina/chloroform: ethyl acetate =100:1-20:1), and 0.78-g refining pigments were obtained. λ_{max} in the inside of chloroform of this phthalocyanine compound was 684 nm. As a result of conducting LC/MS analysis of the compound, molecular ion peak M^+ =1255 was checked.

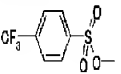

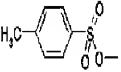
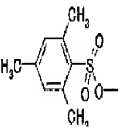
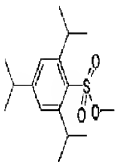
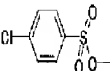
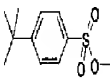
[0031]Comparative example : $\alpha, \alpha, \alpha, \alpha$ -tetrakis (2-methyl phenylthio) zinc phthalocyanine condenser tube in the attached reaction flask 10.0 g of 3-(2-methyl phenylthio) phthalonitrile, It heated teaching and agitating 80 ml of 1-pentanol, and DBU7.6g, the zinc chloride 1.8g was added at 80 **, and it agitated at 100 ** under the nitrogen air current for 5 hours. Heating and churning were stopped, and methanol washed [separation and] the crystal which diluted the reaction mixture with 500 ml of methanol, and deposited, it dried, and 9.2-g crude pigments were obtained. Separation refinement of this crude pigment was carried out with column chromatography, and 4.3-g refining pigments were obtained. λ_{max} in the inside of the carbon tetrachloride of this compound was 720 nm. The extrapolation loss-in-quantity starting temperature measured by TG analysis was 418 **, the extrapolation exothermic starting temperature measured by DSC analysis was 425 **, and the calorific power of the half band width of 25 J/g and an exothermic peak was 30 **.

[0032]As for the degradation starting temperatures of the phthalocyanine compound which has a phenylthio group like the compound of the above-mentioned comparative example, it is common that it is in the range of 350-450 **. On the other hand, degradation starting temperatures are 280 ** and the half band width of DSC of the compound obtained in Embodiment 1 is also as small as 13 **. It turns out that decomposition is low temperature, and this meant having happened with a sufficient response, and pyrolysis characteristics have been sharply improved by changing a phenylthio group into a phenylsulfonyloxy group since the compound of other embodiments was also the same.

[0033]In analyzing the compound of the above embodiment and a comparative example, the following analysis device was used.

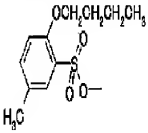
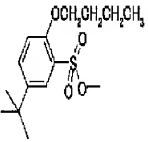
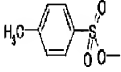
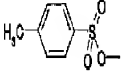

GC/MS: GCMS-QP2000 GFLC/MS by Shimadzu Corp.: The company's LCMS-QP8000IR : Company FTIR-8000PCDSC : Company DSC-50TGA : The company's TGA-50 [0034]

[Table 1]

化合物No.	置換基 R-SO ₃ -	置換位置	中心金属
1		α	VO
2		α	VO
3		α	VO
4		α	VO
5		α	VO
6		α	VO
7		α	VO

[0035]

[Table 2]

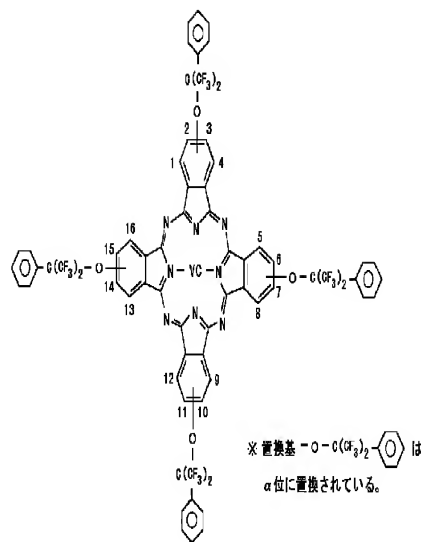
化合物 No.	置換基 R-SO ₂ -	置換位置	中心金属
6		α	V O
9		α	V O
10		α	Z n
11		α	C u
比較例		α	Z n

[0036](Example of a disk-sized experiment)

The substrate which has a 1700-Å-deep guide rail was prepared on the polycarbonate transparent substrate surface (example 120 mm of an experiment in diameter, and 1.2 mm in thickness). Mixed among from the phthalocyanine compound indicated to No.1 with the phthalocyanine compound shown with the following constitutional formula at a rate of 3:7, it was made to dissolve into the mixed solvent which consists of carbon tetrachloride, tetrahydrofuran, 2-butoxyethanol, and methylcyclohexane, and pigment coating liquid was obtained. This pigment liquid was applied on the transparent substrate by the spin coat method, and the optical absorption layer was obtained. The thickness of the optical absorption layer could be about 1500 Å. On the optical absorption layer, by the sputtering process, the silver film was provided by a thickness of about 1000 Å, and the light reflection layer was obtained. Furthermore with the spin coat method, the protective layer which consists of ultraviolet curing resin (Dainippon Ink SD-1700) on a light reflection layer was provided at a thickness of about 5 micrometers, and the recordable compact disc (CD-R) was obtained.

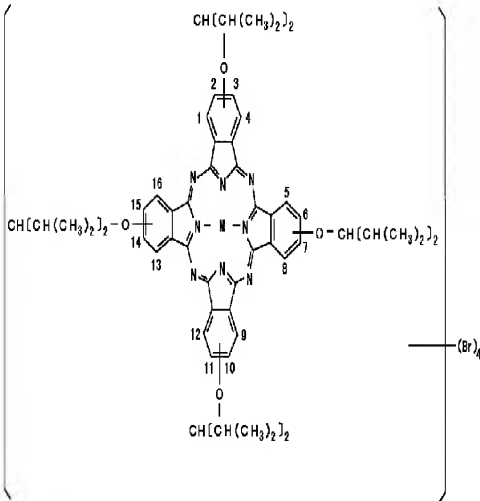
[0037]

[Chemical formula 11]



[0038]The substrate which has a 1700-Å-deep guide rail was prepared on the polycarbonate transparent substrate surface (example 120 mm of comparative experiments in diameter, and 1.2 mm in thickness). The phthalocyanine compound shown with the following constitutional formula was dissolved into the mixed solvent which consists of tetrahydrofuran, 2-butoxyethanol, and methylcyclohexane, and pigment coating liquid was obtained. This pigment liquid was applied on the transparent substrate by the spin coat method, and the optical absorption layer was obtained. The thickness of the optical absorption layer could be about 1500 Å. On the optical absorption layer, by the sputtering process, the silver film was provided by a thickness of about 1000 Å, and the light reflection layer was obtained. Furthermore with the spin coat method, the protective layer which consists of ultraviolet curing resin (Dainippon Ink SD-1700) on a light reflection layer was provided at a thickness of about 5 micrometers, and the recordable compact disc (CD-R) was obtained.

[Chemical formula 12]



[0039]12X CD-R in the above-mentioned example of an experiment and the example of comparative experiments is recorded with commercial CD writer (Shinano Kenshi Co., Ltd. make PX-W124TSi), and the result of having done the error rate, the jitter, and the regeneration test is described below. The following device (instrument) was used for measurement.

Error rate measurement player; CD-CATS (made by Audio Development)

jitter measurement player; -- Philips CD-920JT regeneration test player; -- in CD-R (commercial item) which uses the phthalocyanine mixture concerning RICOH MP708032X A X regeneration this invention, there are few jitters at the time of X12 record, and low good record is possible also for an error rate. Regeneration compatibility is also good. (In addition by CD specification, it is error rate <220 f/s jitter <35ns)

[0040]

[Table 3]

CD-Rサンプル	エラーレート (frame/sec)	3T ビットジッター (ns)	再生テスト
実験例1	2.4	27.5	○再生動作良好
実験例2	2.3	26.0	○再生動作良好
比較実験例	22.8	45.0	△リード遅れあり

[0041]

[Effect of the Invention] Since the phthalocyanine compound of this invention dissolves in various organic solvents easily at a room temperature and the film which is excellent in workability, such as film formation, and was formed has a high absorbancy index and sharp pyrolysis characteristics, utility value is high as added type material for optical recording of a postsript. If the added type optical recording medium of a

postscript is produced using this in order to disassemble especially the phthalocyanine compound of this invention in a narrow temperature span in an instant, even if it records at high speed, the signal of good quality will be acquired.

[Translation done.]

Report Mistranslation

Japanese (whole document in PDF)